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## NEW APPROACH TOWARDS THE DEPOSITION OF I-III-VI THIN FILMS

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## ABSTRACT

The ternary chalcopyrite semiconductor  $\text{Cu}(\text{In}/\text{Ga})(\text{Se}/\text{S})_2$  is currently used as an absorber layer in high efficiency thin film solar cells. In this study, various types of I-III-VI (I = Cu, III = Ga or In, VI = S or Se) thin films ( $\text{CuGaS}_2$ ,  $\text{CuInS}_2$  and  $\text{CuInSe}_2$ ) were prepared from a series of organometallic precursors,  $\text{M}[(\text{S}/\text{Se})_2\text{CNMeR}]_n$  (M = Cu, In, Ga; R = alkyl) by aerosol-assisted chemical vapour deposition (AACVD). In contrast to the metal alkyl compounds,  $\text{MR}_3$  (M = In and Ga; R = alkyl), which are pyrophoric, the precursors are easy to synthesize by one-pot reactions and are air stable. The optimum growth temperature for the preparation of these films on glass substrates using aerosol-assisted chemical vapour deposition (AACVD) was found to be above 400 °C in terms of crystallinity, although deposition does occur at lower temperatures. The films have been characterised using XRPD, SEM and EDS. SEM analyses show all films are microcrystalline. XRPD results show evidence of the crystalline nature of these films. The results of this comprehensive study are presented and discussed.

## INTRODUCTION

Ternary compound semiconductors such as copper indium/gallium disulfide/diselenide ( $\text{CuInS}_2$ ,  $\text{CuGaS}_2$  or  $\text{CuInSe}_2$ ) are promising materials for use in high efficiency solar cells. There have been only a few reports of the deposition of  $\text{CuME}_2$  by CVD methods. A halogen transport VPE method[1] has been used to grow single crystals.  $\text{CuInSe}_2$  films contaminated with  $\text{In}_2\text{Se}_3$  have been deposited by MOCVD using copper(II) hexafluoroacetylacetonate mixed with trimethylamine, triethyl indium and hydrogen selenide.[2,3] A plasma enhanced process using both hexafluoroacetylacetonate copper and indium complexes and a novel selenium source 4-methyl-1,2,3-selenadiazole has also been used.[4] Chichibu has reported[5] the growth of heteroepitaxial layers of  $\text{CuInSe}_2$  using cyclopentadienylcoppertriethylphosphine, trimethyl indium and diethylselenide as the precursors; the first successful MOVPE results.

There are also some initial reports concerning the use of single-source organometallic precursors for the deposition of  $\text{CuInS}_2$  films.[6,7] Recently Hollingsworth *et al.* reported spray CVD of  $\text{CuInS}_2$  films using a single-source precursor,  $(\text{Ph}_3\text{P})_2\text{Cu}(\mu\text{-SEt})_2\text{In}(\text{SEt})_2$ . In their study, highly orientated  $\text{CuInS}_2$  was deposited on Si(111) substrates at 600 °C.[8]

We have been developing a range of dithio- and diseleno-carbamato complexes of various metals which have been successfully used to deposit a wide range of semiconductor materials.[9] One particularly successful modification to the sulfur/selenium containing ligands has been to develop compounds in which the parent amine is asymmetrically substituted and involves a bulky or extended alkyl substituent.[10,11] Compounds with these ligands are air stable and sufficiently volatile for the deposition of thin films of materials such as  $\text{Cu}_2\text{E}$ ,  $\text{In}_2\text{E}_3$ ,  $\text{Ga}_2\text{E}_3$ ,  $\text{ZnE}$

and CdE (E = S or Se).[12-13] Success with the binary parents of CuInE<sub>2</sub> has encouraged us to deposit the ternary phase. In this paper we report a simple AACVD process for copper indium/gallium disulfide/diselenide thin films.

## EXPERIMENTAL DETAILS

### Precursor Synthesis

The precursors were prepared by literature methods[14] and analyzed by CHN, NMR, Mass Spec. and TGA.

**Cu(S<sub>2</sub>CNMe<sup>n</sup>Hex)<sub>2</sub> (1):** Yield 64%, m.p. 48 °C, Elemental analysis: C<sub>16</sub>H<sub>32</sub>S<sub>4</sub>N<sub>2</sub>Cu. Calculated: C: 43.29, H: 7.2, N: 6.05%. Found: C: 42.76, H: 6.97, N: 6.05%. Mass Spectrum: m/z significant peaks [M<sup>+</sup>] 444, [CuS<sub>2</sub>CNCH<sub>3</sub>C<sub>6</sub>H<sub>13</sub>] 253, [S<sub>2</sub>CNCH<sub>2</sub>CH] 117, [S<sub>2</sub>CNCH<sub>2</sub>C] 116.

**In(S<sub>2</sub>CNMe<sup>n</sup>Hex)<sub>3</sub> (2):** Yield 67%, m. p. 100 °C, Elemental analysis: C<sub>24</sub>H<sub>48</sub>N<sub>3</sub>S<sub>6</sub>In. Calculated: C: 42.02, H: 6.91, N: 5.88%. Found: C: 42.27, H: 6.73, N: 6.01%. <sup>1</sup>H NMR (δ, C<sub>6</sub>D<sub>6</sub>, 300 MHz): 0.86 (t, 9H, -NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.18 (m, 18H, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.38 (m, 6H, -NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 2.8 (s, 9H, -NCH<sub>3</sub>), 3.3 (t, 6H, -NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>).

**Cu(Se<sub>2</sub>CNMe<sup>n</sup>Hex)<sub>2</sub> (3):** Yield 70%, Elemental analysis: C<sub>16</sub>H<sub>32</sub>Se<sub>4</sub>N<sub>2</sub>Cu. Calculated: C: 30.45, H: 5.07, N: 4.44%. Found: C: 30.84, H: 5.65, N: 4.45%. Mass Spectrum: m/z significant peaks, [CuSe<sub>2</sub>CNCH<sub>3</sub>CH<sub>2</sub>C] 288, [CuSe<sub>2</sub>CNCCH<sub>2</sub>CH<sub>2</sub>CH] 300, [CuSe<sub>2</sub>CNCHCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>C] 314.

**In(Se<sub>2</sub>CNMe<sup>n</sup>Hex)<sub>3</sub> (4):** Yield 57%, Elemental analysis: C<sub>24</sub>H<sub>48</sub>N<sub>3</sub>Se<sub>6</sub>In. Calculated: C: 29.81, H: 4.96, N: 4.35%. Found: C: 30.83, H: 4.97, N: 4.40%. <sup>1</sup>H NMR (δ, C<sub>6</sub>D<sub>6</sub>, 300 MHz): δ 0.55 (t, 9H, -NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 0.77 (m, 18H, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.00 (m, 6H, -NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 2.4 (s, 9H, -NCH<sub>3</sub>), 2.9 (t, 6H, -NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>).

**Ga(S<sub>2</sub>CNMe<sup>n</sup>Hex)<sub>3</sub> (5):** Yield 68% m. p. 85 °C, Elemental analysis: C<sub>24</sub>H<sub>48</sub>N<sub>3</sub>S<sub>6</sub>Ga Calculated: C: 44.99, H: 7.55, N: 6.56% Found: C: 44.78, H: 8.14, N: 6.58%, <sup>1</sup>H NMR (δ, C<sub>6</sub>D<sub>6</sub>, 300 MHz): δ 0.92 (t, 9H, -NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.18 (m, 18H, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.40 (m, 6H, -NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 2.8 (s, 9H, -NCH<sub>3</sub>), 3.4 (t, 6H, -NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>).

### Deposition of films and characterizations

**Aerosol Assisted Chemical Vapour Deposition (AACVD):** Approximately 0.25g of precursor was dissolved in 30ml Toluene (or THF) in the round-bottomed flask. Six glass substrates (1 × 2 cm) were placed inside the reactor tube. The carrier gas flow rate was controlled by Platon flow gauges. The solution in the flask is placed in a water bath above the piezoelectric modulator of a humidifier, where aerosol droplets are generated and transferred by the carrier gas into a hot-wall zone. Then both the solvent and the precursor evaporate and the precursor vapour reaches the heated substrate surface where thermally induced reactions and film deposition take place. This homemade aerosol-assisted chemical vapour deposition kit consists of a two-neck flask, a PIFCO ultrasonic humidifier (Model No. 1077) and a CARBOLITE furnace.

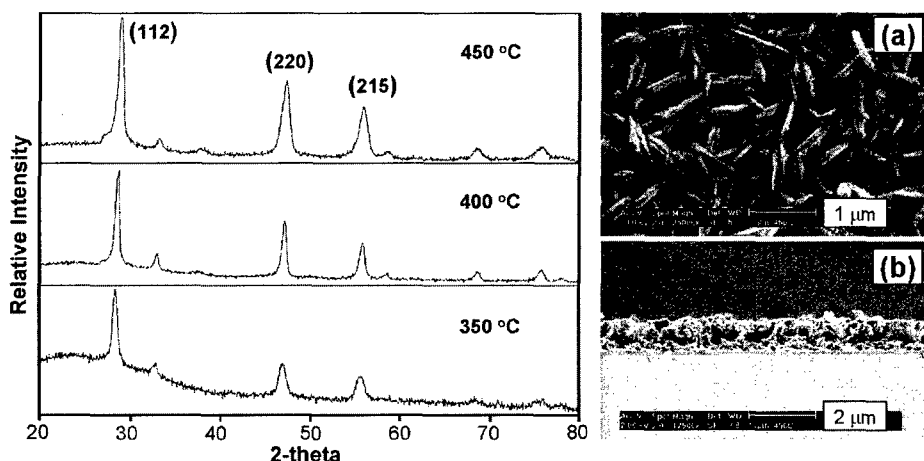
**Film characterizations:** X-ray diffraction studies were performed using  $\text{Cu-K}\alpha$  radiation on a Philips X'Pert MPD diffractometer. The sample was mounted flat and scanned from  $20 - 80^\circ$  in steps of  $0.04^\circ$  with a count time of 2 s. Samples were carbon coated before electron microscopic analysis. All EDS and electron microscopy was then carried out in a Jeol Superprobe 733 microscope.

## RESULTS AND DISCUSSION

### Copper Indium Sulfide by AACVD

Films of  $\text{CuInS}_2$  were successfully grown on glass at  $350 - 450^\circ\text{C}$  by AACVD. It is interesting to note that employing AACVD can reduce deposition temperature for the growth of  $\text{CuInS}_2$  to  $350^\circ\text{C}$  as compared to those grown by LP-MOCVD.[15] All films grown using compounds **1** and **2** (1:1 ratio) gave narrow and strong peaks in the X-ray powder diffraction and show characteristic tetragonal phase of  $\text{CuInS}_2$  (Fig. 1). The XRPD patterns of the films grown at various growth temperatures show a preferred orientation along the (112) plane regardless of growth temperature. EDS analysis of films grown at  $450^\circ\text{C}$  peaks corresponding to Cu, In and S and ratio was found to be close to 1:1:2.

SEM analysis for the as-deposited  $\text{CuInS}_2$  films on glass indicates slightly different features in terms of their morphology compared to those grown by LP-MOCVD. Films grown at  $450^\circ\text{C}$  show that particles are formed as randomly orientated flakes *ca.*  $0.2\ \mu\text{m}$  thick as compared to the relatively thick width (*ca.*  $1\ \mu\text{m}$ ) crystallites grown by LP-MOCVD and particles grown by AACVD are laid down horizontally on the glass substrate. Also the shape of particles are very similar to those prepared on fused silica using  $(\text{Ph}_3\text{P})_2\text{CuIn}(\text{SEt})_4$  by spray CVD.[8]



**Fig. 1.** XRPD patterns of  $\text{CuInS}_2$  on glass [using compounds **1** and **2** by AACVD (temperatures indicate growth temperatures)] and SEM images of the films grown at  $450^\circ\text{C}$ .

In 2 hour growth, films were found to be *ca.* 1  $\mu\text{m}$  thick with 0.5  $\mu\text{m}/\text{h}$  growth rate. At lower growth temperature (350  $^{\circ}\text{C}$ ), a mixture of morphologies can be seen. Particle size is found to be between 0.5 – 1.6  $\mu\text{m}$ .

Various ratios of compounds **1** and **2** were also utilized in order to investigate stoichiometric change of  $\text{CuInS}_2$  films. XRPD patterns of as-deposited films grown with different ratios show that there is no evidence to trace any by-products such as indium sulfide or copper sulfide and indicate no effect on stoichiometry of  $\text{CuInS}_2$ , in contrast to the LP-MOCVD work.

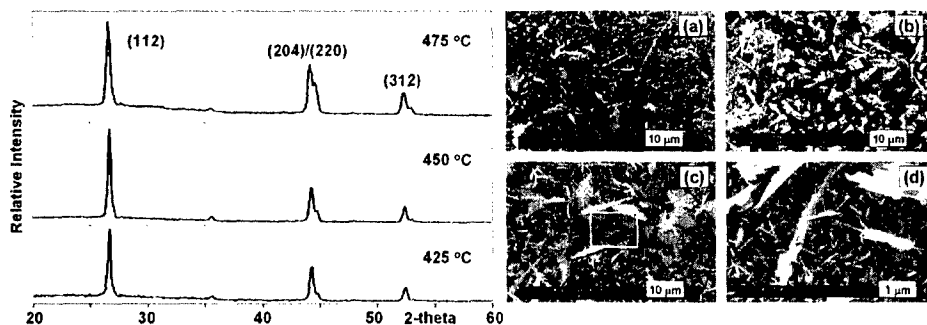
### Copper Indium Selenide by AACVD

$\text{CuInSe}_2$  films have been also deposited on glass using compounds **3** and **4** by AACVD. In this case, only a 1:1 molar ratio of compounds **3** and **4** was used. Films were grown at 425 – 475  $^{\circ}\text{C}$  with constant argon flow rate of 180 sccm. XRPD analyses (Fig. 2) suggest that as-deposited films have tetragonal phase with a preferred orientation along (112) direction in all cases.

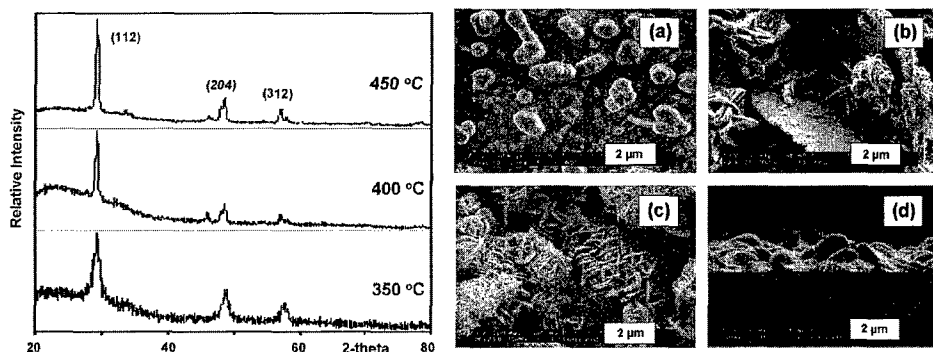
SEM images of the films show (Fig. 2) that the deposited layer is not homogenous and mainly consist of several different shapes of particles with a poor coverage at lower growth temperature (425  $^{\circ}\text{C}$ ). The heterogeneous morphology on thin film layer can be altered by using single crystalline substrates such as  $\text{InP}(111)$  and  $\text{Si}(111)$  which may lead to homogenous growth process. The observation of homogenous growth was found in the LP-MOCVD study.[16]

### Copper Gallium Sulfide by AACVD

In the growth of  $\text{CuGaS}_2$ , stoichiometric amount of compounds **1** and **5** were employed and dissolved in THF (30ml). In initial experiments, Cu/In ratio was maintained at 1:1 and growth time was kept constant for 2 hours (180 sccm/flow rate).



**Fig. 2.** XRPD patterns of  $\text{CuInSe}_2$  films on glass by AACVD and SEM images of  $\text{CuInSe}_2$  on glass using compounds **3** and **4** by AACVD [(a) 425  $^{\circ}\text{C}$ ; (b) 450  $^{\circ}\text{C}$ ; (c) and (d) 475  $^{\circ}\text{C}$ ].



**Fig. 3.** XRPD patterns of  $\text{CuGaS}_2$  films on glass by AACVD and SEM images of  $\text{CuGaS}_2$  on glass using compounds **1** and **5** by AACVD [(a) 300 °C; (b) 400 °C; (c) and (d) 450 °C].

XRPD patterns (Fig. 3) show that deposited films by AACVD have chalcopyrite structure with a preferred orientation along (112) direction (JCPDS 27-0279). It is also conclusive that at high temperatures, the crystallinity of deposited film is highly indicated by the sharpness of peaks, whilst at low temperature (350 °C) XRPD pattern exhibits weak reflections indicating poorly crystalline films. Similar results are obtained for the films grown at lower argon flow rate (120 sccm).

SEM analysis (Fig. 3) shows that the material consists of clusters of randomly orientated platelets to the surface for films grown at 400 and 450 °C (180 sccm/flow rate). The films deposited are dense but are uneven. Growth rates are approximately 500 nm/h for films grown at 350 °C and 1  $\mu\text{m}/\text{h}$  at 450 °C. As growth temperature decrease, the growth of  $\text{CuGaS}_2$  is significantly reduced. EDS analysis shows films are slightly copper rich with Cu 30%, Ga 24% and S 46%. However, when flow rate of argon as a carrier gas was reduced to 120 sccm, the clusters formed tended to be denser but some individual platelets can also be seen. In 2 hour growth at 450 °C, films with *ca.* 1.5  $\mu\text{m}$  thickness were deposited on the glass substrate (growth rate, *ca.* 0.75  $\mu\text{m}/\text{h}$ ). EDS elemental atomic percent for  $\text{CuGaS}_2$  films was found to be 29%, 23% and 48% respectively.

## CONCLUSIONS

The results described herein demonstrate that AACVD using organometallic precursors results in stoichiometric  $\text{CuME}_2$  ( $\text{M} = \text{In}$  or  $\text{Ga}$ ,  $\text{E} = \text{S}$  or  $\text{Se}$ ) films, and the quality (e.g. morphology or preferred orientations) of films are dependent on experimental parameters. Furthermore, films grown on glass by AACVD show similar XRPD patterns regardless deposited materials. It is evident that the AACVD approach leads to the deposition of I-III-IV films from the precursors used in this work. As a result, it is shown to be that a series of asymmetrical alkyldithiocarbamate metal complexes can be used as precursors for the deposition of I-III-VI class films by CVD techniques.

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